Supporting Information

Total Synthesis of CRM646-A and B, Two Fungal Glucuronides with Potent Heparinase Inhibition Activities

Ping Wang, Zhaojun Zhang, Biao Yu*

State Key Laboratory of Bioorganic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, China. Fax: (0086)-21-64166128

Email: byu@mail.sioc.ac.cn

S1-S4 List of the contents

S5—S19 Experimental Section

S5 Methyl (2,3,4-tri-O-acetyl-D-glucopyranosyl (N-phenyl)trifluoroacetimidate)uronate (4)

S5 Benzyl (2,3,4-tri-O-acetyl-D-glucopyranosyl trichloroacetimidate)uronate (5)

S6 Benzyl (2,3,4-tri-O-acetyl-D-glucopyranosyl (N-phenyl)trifluoroacetimidate)uronate (6)

S7 2,4-Dihydroxy-6-methylbenzaldehyde (9)

S7 Benzyl 2,4-dihydroxy-6-methylbenzoate (11)

S8 2,4-Dimethoxy-6-methylbenzaldehyde (12)

S8 2,4-Dimethoxy-6-methylbenzoic acid (13)

S9 Ethyl 2,4-dimethoxy-6-methylbenzoate (14b)

S9 Ethyl 2,4-dimethoxy-6-pentadecanlybenzoate (15b)

S10 Ethyl 2,4-dihydroxy-6-pentadecanlybenzoate (16) and Ethyl 2-hydroxy-4-methoxy-6-pentadecanlybenzoate (17)

S11 2,4-Bis(benzyloxy)-6-pentadecanlybenzoic acid (19)

S12 Benzyl 4’-(2,4-dibenzyloxy-6-pentadecanlybenzoyloxy)-2’-hydroxy-6’-methylbenzoate (20)
S12 4’-(2,4-Dihydroxy-6-pentadecanylbenzoyloxy)-2’-hydroxy-6’-methylbenzoic acid (21)

S13 Benzyl 4’-(2,4-dihydroxy-6-pentadecanylbenzoyloxy)-2’-hydroxy-6’-methylbenzoate (22)

S14 Benzyl 4’-(4-O-(2”’,3”’-di-O-acetyl-4”’-O-benzylidene-β-D-glucopyranosyl)-2-hydroxy-6-pentadecanylbenzoyloxy)-2’-hydroxy-6’-methylbenzoate (23)

S15 Benzyl 4’-(4-O-(2”’,3”’-di-O-acetyl-4”’-O-benzylidene-β-D-glucopyranosyl)-2-benzyloxy-6-pentadecanylbenzoyloxy)-2’-benzyloxy-6’-methylbenzoate (24)

S15 Benzyl 4’-(4-O-(2”’,3”’-di-O-acetyl-β-D-glucopyranosyl)-2-benzyloxy-6-pentadecanylbenzoyloxy)-2’-benzyloxy-6’-methylbenzoate (25)

S16 2,4-Dihydroxy-6-pentadecanylbenzoic acid (26)

S17 Benzyl 2,4-dihydroxy-6-pentadecanylbenzoate (27)

S17 Benzyl 2-hydroxy-4-(methoxymethoxy)-6-methylbenzoate (28)

S18 Benzyl 2-(benzyloxy)-4-(methoxymethoxy)-6-methylbenzoate (29)

S18 Benzyl 2-(benzyloxy)-4-hydroxy-6-methylbenzoate (30)

S20---S67 1H and 13C NMR spectra

S20 1H NMR spectrum of Methyl (2,3,4-tri-O-acetyl-D-glucopyranosyl (N-phenyl)trifluoroacetimidate)uronate (4)

S21 13C NMR spectrum of 4

S22 1H NMR spectrum of Benzyl (2,3,4-tri-O-acetyl-D-glucopyranosyl trichloroacetimidate)uronate (5)

S23 13C NMR spectrum of 5

S24 1H NMR spectrum of Benzyl (2,3,4-tri-O-acetyl-D-glucopyranosyl (N-phenyl)trifluoroacetimidate)uronate (6)

S25 13C NMR spectrum of 6

S26 1H NMR spectrum of ethyl 2,4-dihydroxy-6-pentadecanlybenzoate (16)

S27 13C NMR spectrum of 16

S28 1H NMR spectrum of ethyl 2-hydroxy-4-methoxy-6-pentadecanlybenzoate (17)

S29 13C NMR spectrum of 17

S30 1H NMR spectrum of ethyl 2,4-dibenzyloxy-6-pentadecanlybenzoate (18)

S31 1H NMR spectrum of 2,4-Bis(benzyloxy)-6-pentadecanlybenzoic acid (19)
S32 $^{13}$C NMR spectrum of 19
S33 $^1$H NMR spectrum of benzyl 4’-(2,4-dibenzyloxy-6-pentadecanylbenzoyloxy)-2’-hydroxy-6’-methylbenzoate (20)
S34 $^{13}$C NMR spectrum of 20
S35 $^1$H NMR spectrum of 4’-(2,4-dihydroxy-6-pentadecanylbenzoyloxy)-2’-hydroxy-6’-methylbenzoic acid (21)
S36 $^1$H NMR spectrum of benzyl 4’-(2,4-dihydroxy-6-pentadecanylbenzoyloxy)-2’-hydroxy-6’-methylbenzoate (22)
S37 $^{13}$C NMR spectrum of 22
S38 $^1$H NMR spectrum of benzyl 4’-(4-O-(2’’’,3’’’-di-O-acetyl-4’’’,6’’’-O-benzylidene-\(\beta\)-D-glucopyranosyl)-2-hydroxy-6-pentadecanylbenzoyloxy)-2’-hydroxy-6’-methylbenzoate (23)
S39 $^1$H NMR spectrum of benzyl 4’-(4-O-(2’’’,3’’’-di-O-acetyl-4’’’,6’’’-O-benzylidene-\(\beta\)-D-glucopyranosyl)-2-benzyloxy-6-pentadecanylbenzoyloxy)-2’-benzyloxy-6’-methylbenzoate (24)
S40 $^{13}$C NMR spectrum of 24
S41 $^1$H NMR spectrum of benzyl 4’-(4-O-(2’’’,3’’’-di-O-acetyl-\(\beta\)-D-glucopyranosyl)-2-benzyloxy-6-pentadecanylbenzoyloxy)-2’-benzyloxy-6’-methylbenzoate (25)
S42 $^{13}$C NMR spectrum of 25
S43 $^1$H NMR spectrum of benzyl 2,4-dihydroxy-6-pentadecanylbenzoate (27)
S44 $^{13}$C NMR spectrum of 27
S45 $^1$H NMR spectrum of benzyl 2-hydroxy-4-(methoxymethoxy)-6-methylbenzoate (28)
S46 $^{13}$C NMR spectrum of 28
S47 $^1$H NMR spectrum of benzyl 2-(benzyloxy)-4-(methoxymethoxy)-6-methylbenzoate (29)
S48 $^{13}$C NMR spectrum of 29
S49 $^1$H NMR spectrum of benzyl 2-(benzyloxy)-4-hydroxy-6-methylbenzoate (30)
S50 $^{13}$C NMR spectrum of 30
S51 $^1$H NMR spectrum of 4-O-(methyl 2’,3’,4’-tri-O-acetyl-\(\beta\)-D-glucopyranosyluronate)-2-hydroxy-6-pentadecanylbenzoyloxy-benzoic acid (32)
S52 \(^{13}\text{C}\) NMR spectrum of \(32\)
S53 \(^1\text{H}\) NMR spectrum of benzyl 4’-(4-\(O\)-(methyl 2”’,3”’,4”’-tri-\(O\)-acetyl-\(\beta\)-D-glucopyranosyluronate))-2-hydroxy-6-pentadecanlybenzoyloxy)-2’-benzyloxy-6’-methylbenzoate (33)
S54 \(^{13}\text{C}\) NMR spectrum of \(33\)
S55 \(^1\text{H}\) NMR spectrum of benzyl 4’-(4-\(O\)-(methyl 2”’,3”’,4”’-tri-\(O\)-acetyl-\(\beta\)-D-glucopyranosyluronate)-2-benzyloxy-6-pentadecanlybenzoyloxy)-2’-benzyloxy-6’-methylbenzoate (34)
S56 \(^{13}\text{C}\) NMR spectrum of \(34\)
S57 \(^1\text{H}\) NMR spectrum of Benzyl 4’-(4-\(O\)-(\(\beta\)-D-glucopyranosyluronic acid))-2-benzyloxy-6-pentadecanlybenzoyloxy)-2’-benzyloxy-6’-methylbenzoate (35)
S58 \(^1\text{H}\) NMR spectrum of benzyl 4-\(O\)-(methyl 2’,3’,4’-tri-\(O\)-acetyl-\(\beta\)-D-glucopyranosyluronate)-2-benzyloxy-6-pentadecanlybenzoyloxy-benzoate (36)
S59 \(^{13}\text{C}\) NMR spectrum of \(36\)
S60 \(^1\text{H}\) NMR spectrum of benzyl 4-\(O\)-(methyl \(\beta\)-D-glucopyranosyluronate)-2-benzyloxy-6-pentadecanlybenzoyloxy-benzoate (37)
S61 \(^{13}\text{C}\) NMR spectrum of \(37\)
S62 \(^1\text{H}\) NMR spectrum of benzyl 4’-(4-\(O\)-(methyl \(\beta\)-D-glucopyranosyluronate)-2-hydroxy-6-pentadecanlybenzoyloxy)-2’-benzyloxy-6’-methylbenzoate (39)
S63 \(^{13}\text{C}\) NMR spectrum of \(39\)
S64 \(^1\text{H}\) NMR spectrum of CRM646-A (1)
S65 \(^{13}\text{C}\) NMR spectrum of CRM646-A (1)
S66 \(^1\text{H}\) NMR spectrum of CRM646-B (2)
S67 \(^{13}\text{C}\) NMR spectrum of CRM646-B (2)
Experimental Section

General Remarks. Solvents were distilled from the appropriate drying agents before use. Unless stated otherwise, all reactions were carried out under a positive pressure of argon and were monitored by TLC on silica gel (0.5 mm). Spots were detected under UV light or by charging with 10% H₂SO₄ in MeOH. Flash column chromatography was carried out on silica gel (400 mesh).

Methyl (2,3,4-tri-O-acetyl-D-glucopyranosyl (N-phenyl)trifluoroacetimidate)uronate (4)

A suspension of methyl 2,3,4-tri-O-acetyl-D-glucopyranose uronate (500 mg, 1.44 mmol), K₂CO₃ (398 mg, 2.38 mmol), and N-phenyl trifluoroacetimidoyl chloride (0.25 mL) in CH₂Cl₂ (10 mL) was stirred at ambient temperature overnight. The mixture was filtered with washing with CH₂Cl₂. The filtrates were concentrated under vacuo to give a residue, which was purified by silica gel column chromatography (petroleum ether : EtOAc = 5:1) to afford 4 (749 mg, 99%) as a white foam. Rf = 0.24 (petroleum ether : EtOAc = 4:1); α : β = 0.88 (estimated by ¹H NMR); ¹H NMR (300 MHz, CDCl₃): δ 7.24 (t, J = 6.0 Hz, 2 H), 7.07 (d, J = 6.6 Hz, 1 H), 6.78, 6.72 (2 d, J = 7.4 Hz, 2 H), 6.57, 5.88 (2 br s, 1 H), 5.54, 5.25-5.10 (t + m, J = 9.5 Hz, 3 H), 4.40, 4.08 (d + br s, J = 9.6 Hz, 1 H), 3.69 (s, 3 H), 2.00, 1.99, 1.97 (3 s, 9 H); ¹³C NMR (75 MHz, CDCl₃): δ 169.5, 169.4, 169.3, 169.2, 169.0, 168.7, 166.8, 166.7, 142.6, 142.5, 128.6, 128.5, 124.5, 124.4, 119.0, 93.8, 91.7, 72.6, 70.7, 70.2, 69.8, 68.9, 68.7, 68.2, 52.7, 52.6, 20.2, 20.1; ESI-MS (m/z) for C₂₁H₂₂F₃NO₁₀ [M + Na⁺]: 528.1; Anal. Calcld for C₂₁H₂₂F₃NO₁₀·H₂O: C, 48.19; H, 4.62; N, 2.68. Found: C, 48.36; H, 4.36; N, 2.49.

Benzyl (2,3,4-tri-O-acetyl-D-glucopyranosyl trichloroacetimidate)uronate (5)
A suspension of benzyl 2,3,4-tri-O-acetyl-D-glucopyranose uronate (300 mg, 0.73 mmol), K$_2$CO$_3$ (250 mg), and NCCl$_3$ (0.25 mL) in CH$_2$Cl$_2$ (10 mL) was stirred at ambient temperature overnight. The mixture was filtered with washing with CH$_2$Cl$_2$. The filtrates were concentrated under vacuo to give a residue, which was purified by silica gel column chromatography (petroleum ether : EtOAc = 5:1) to afford 5 (178 mg, 44%) as a white foam. $R_f = 0.29$ (petroleum ether : EtOAc = 4:1); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.75 (s, 1 H, NH), 7.37 (s, 5 H, PhH), 6.66 (d, $J$ = 3.9 Hz, 1 H, H-1), 5.62 (t, $J$ = 9.8 Hz, 1 H, H-3), 5.27 (t, $J$ = 9.8 Hz, 1 H, H-4), 5.16 (dd, $J$ = 9.8, 4.1 Hz, 1 H, H-2), 5.15 (s, 2 H, PhCH$_2$), 4.54 (d, $J$ = 10.5 Hz, 1 H, H-5), 2.04, 2.02, 1.79 (3 s, 9 H, 3 Ac); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 169.7, 169.6, 169.3, 166.6, 160.5, 134.5, 128.8, 128.7, 128.6, 92.6, 70.6, 69.4, 69.0, 68.0, 20.5, 20.3, 20.2; ESIMS ($m/z$): 576.0 (M + K$^+$); HR-ESIMS ($m/z$) Calcd for C$_{30}$H$_{30}$O$_7$Na$: 575.9980$; Found: 575.9992.

**Benzyl (2,3,4-tri-O-acetyl-D-glucopyranosyl (N-phenyl)trifluoroacetimidate)uronate (6)**

A suspension of benzyl 2,3,4-tri-O-acetyl-D-glucopyranose uronate (180 mg, 0.44 mmol), K$_2$CO$_3$ (121 mg, 0.88 mmol), and N-phenyl trifluoroacetimidoyl chloride (0.10 mL) in CH$_2$Cl$_2$ (10 mL) was stirred at ambient temperature overnight. The mixture was filtered with washing with CH$_2$Cl$_2$. The filtrates were concentrated under vacuo to give a residue, which was purified by silica gel column chromatography (petroleum ether : EtOAc = 5:1) to afford 6 (250 mg, 97%) as a white foam. $R_f = 0.32$ (petroleum ether : EtOAc = 3:1); $\alpha : \beta = 1.20$ (estimated by $^1$H NMR); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.39-6.76 (m, 10 H), 6.68, 5.94 (2br, s, 1 H, H-1$\beta$, $\alpha$), 5.59 (t, $J$ = 9.9 Hz, 0.55 H), 5.33-5.14 (m, 4.45 H), 4.51 (d, $J$ = 9.6 Hz, 0.55 H), 4.18 (d, $J$ = 10.0 Hz, 0.45 H), 2.09, 2.08, 2.05, 2.03, 1.82, 1.81 (6
$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 12.38 (s, 1 H, OH-2), 10.10 (s, 1 H, -CHO), 6.22 (s, 2 H, H-3, H-5), 5.50 (s, 1 H, OH-4), 5.50 (s, 1 H, OH-4), 2.53 (s, 3 H, Me).

**Benzyl 2,4-dihydroxy-6-methylbenzoate (11)**

To a solution of 9 (3.78 g, 24.8 mmol) and NaH$_2$PO$_4$ (7.47 g, 2.5 eq) in DMSO (50.0 mL) and water (12.5 mL) at 0 °C, was slowly added a solution of NaClO$_2$ (80%, 5.4 g) in H$_2$O (12 mL). The mixture was stirred at room temperature overnight, and then saturated aqueous Na$_2$CO$_3$ (25 mL) was added. The mixture was extracted with EtOAc (15 mL). The aqueous phase was acidified to pH = 1 with concentrated HCl, and then was extracted with EtOAc (50 mL $\times$ 3). The combined organic phases were washed with
water (50 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, and then filtered, and concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether : EtOAc = 3:1 → 2:1) to give acid 10 (3.21 g, 77%) as a pale yellow solid. R\textsubscript{f} 0.25 (petroleum ether : AcOEt = 2:1); \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{3}OD): δ 10.06 (s, 1 H, OH), 6.19 (s, 1 H, ArH), 6.14 (s, 1 H, ArH), 4.89 (br s, 1 H, OH), 2.48 (s, 3 H, Me).

A suspension of 10 (200 mg, 1.19 mmol), BnBr (0.16 mL, 1.07 eq), and KHCO\textsubscript{3} (143 mg, 1.33 eq) in DMF (10 mL) was stirred at ambient temperature overnight. After quenching the reaction with ice water, the mixture was extracted with EtOAc (50 mL × 3). The organic phase was washed with water (30 mL × 2) and dried over Na\textsubscript{2}SO\textsubscript{4}. The filtrates were concentrated under vacuo to give a residue, which was purified by silica gel column chromatography (petroleum ether : EtOAc = 8:1) to afford 11 (240 mg, 78%) as a white solid. R\textsubscript{f} 0.51 (petroleum ether : EtOAc = 4:1). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): δ 11.76 (s, 1 H, OH), 7.42-7.37 (m, 5 H, PhH), 6.28 (d, \textit{J} = 2.4 Hz, 1 H, ArH), 6.21 (d, \textit{J} = 2.4 Hz, 1 H, ArH), 5.38 (s, 2 H, OCH\textsubscript{2}), 2.47 (s, 3 H, Me).

2,4-Dimethoxy-6-methylbenzaldehyde (12)

\[ \text{CHO} \]

\[ \text{OMe} \]

\[ \text{MeO} \]

\[ \text{OMe} \]

\[ \text{12} \]

A mixture of 9 (3.84 g, 25.2 mmol), K\textsubscript{2}CO\textsubscript{3} (14.0 g, 4.0 eq), and MeI (4.7 mL, 3.0 eq) in dry acetone (30 mL) was heated to reflux over 8 h. The mixture was filtered to move K\textsubscript{2}CO\textsubscript{3} and concentrated. The residue was dissolved in EtOAc (360 mL), and washed with water (35 mL × 3). The organic layer was dried over Na\textsubscript{2}SO\textsubscript{4} and evaporated at reduced pressure to afford 12 as a yellow powder (4.54 g, 100%). R\textsubscript{f} 0.50 (petroleum ether : AcOEt = 4:1); \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): δ 10.48 (s, 1 H, -CHO), 6.32 (s, 2 H, H-3, H-5), 3.88 (s, 3 H, 2 × OMe), 2.58 (s, 3 H, Me).

2,4-Dimethoxy-6-methylbenzoic acid (13)
To a mixture of aldehyde 12 (4.54 g, 25.2 mmol) and NaH$_2$PO$_4$ (7.59 g, 2.5 eq) in DMSO (118 mL) and H$_2$O (15 mL), was slowly added NaClO$_2$ (80%, 6.84 g, 2.4 eq) in H$_2$O (10 mL). After stirring at rt overnight, saturated aqueous Na$_2$CO$_3$ (50 mL) was added. The resulting solution was extracted with EtOAc (15 mL). The aqueous phase was acidified to pH = 1 with concentrated HCl and then extracted with EtOAc (50 mL × 3). The combined organic phase was washed with water (50 mL), dried over Na$_2$SO$_4$, and then filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (petroleum ether : EtOAc = 3:1 → 2:1) to give 13 (4.15 g, 84%) as a white powder.

**Ethyl 2,4-dimethoxy-6-methylbenzoate (14b)**

A solution of acid 13 (2.67 g, 13.6 mmol), DBU (3.7 mL, 1.5 eq), and EtI (5.1 mL, 2.0 eq) in dry CH$_3$CN (40 mL) was stirred overnight at room temperature. The solvent was evaporated. The residue was applied to silica gel column chromatography (petroleum ether: EtOAc = 7:1) to give 14b (3.02 g, 99%) as a colorless oil. R$_f$ 0.32 (petroleum ether: EtOAc = 8:1); $^1$H NMR (300 MHz, CDCl$_3$): δ 6.32 (s, 2 H, ArH), 4.37 (q, $J = 6.9$ Hz, 2 H, OCH$_2$), 3.80 (s, 6 H, 2 × OMe), 2.30 (s, 3 H, ArCH$_3$), 1.37 (t, $J = 7.2$ Hz, 3 H, -CH$_2$Me).

**Ethyl 2,4-dimethoxy-6-pentadecanylbenzoate (15b)**
To a stirred solution of LDA at –78 °C, prepared from diisopropylamine (1.75 mL, 1.3 eq) and n-BuLi (7.6 mL, 1.3 eq, 1.6 M solution in hexane) in dry THF (20 mL) under Ar at 0 °C, was slowly added 14b (2.226 g, 9.93 mmol, in 10 mL dry THF) for 20 min. Then CH$_3$(CH$_2$)$_{12}$CH$_2$Br (3.89 mL, 1.5 eq, in 5 mL THF) was added to the anion solution. After stirring at -78 °C for 3 h, the cooling bath was removed and stirring continued overnight. The mixture was acidified to pH = 1 with 1 N HCl, and then was extracted with EtOAc (50 mL × 2). The organic phase was washed with brine (50 mL × 2), dried over Na$_2$SO$_4$, and concentrated. The residue was applied to silica gel column chromatography (petroleum ether: EtOAc = 7:1) to give 15b (2.92 g, 70%) as a colorless oil. R$_f$ 0.36 (petroleum ether: EtOAc = 7:1); $^1$H NMR (300 MHz, CDCl$_3$): δ 6.33 (d, $J$ = 2.4 Hz, 1 H, ArH), 6.32 (d, $J$ = 1.5 Hz, 1 H, ArH), 4.37 (q, $J$ = 7.2 Hz, 2 H, OCH$_2$), 3.81 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), 2.55 (t, $J$ = 8.0 Hz, 2 H, ArCH$_2$), 1.58 (br, 2 H, ArCH$_2$CH$_2$), 1.37 (t, $J$ = 7.1 Hz, 3 H, CO$_2$CH$_2$Me), 1.26 (m, 24 H, Ar(CH$_2$)$_{12}$), 0.88 (t, $J$ = 6.6 Hz, 3 H, Ar(CH$_2$)$_{14}$Me).

Ethyl 2,4-dihydroxy-6-pentadecanylbenzoate (16) and Ethyl 2-hydroxy-4-methoxy-6-pentadecanylbenzoate (17)

To a solution of 15b (1.53 g, 3.52 mmol) in dry CH$_2$Cl$_2$ (30 mL) at –78 °C was slowly added BBr$_3$ (3.52 mL, 2.1 eq, 2.1 M in CH$_2$Cl$_2$). The resulting mixture was warmed up to –10 °C. After stirring for 48 h, the mixture was quenched with ice water (100 mL). The aqueous phase was extracted with CH$_2$Cl$_2$ (50 mL × 2). The combined organic phase was washed with brine (50 mL × 2), dried over Na$_2$SO$_4$, and then concentrated. The residue was applied to silica gel column chromatography (petroleum ether: EtOAc = 6:1) to give 16 (1.20 g, 82%) and 17 (228 mg, 17%) as white solids. Compound 16: R$_f$ 0.31 (petroleum ether: EtOAc = 7:1); $^1$H NMR (300 MHz, CDCl$_3$): δ 11.90 (s, 1 H, OH), 6.27 (d, $J$ = 2.1 Hz, 1 H, ArH), 6.22 (d, $J$ = 2.7 Hz, 1 H, ArH), 5.14 (br s, 1 H, OH), 4.39 (q, $J$ = 7.2 Hz, 2 H, OCH$_2$), 2.84 (t, $J$ = 7.7 Hz, 2 H, ArCH$_2$), 1.53...
(m, 2 H, ArCH₂CH₂), 1.40 (t, J = 7.1 Hz, 3 H, OCH₂Me), 1.24 (m, 24 H, Ar(CH₂)₂(CH₂)₁₂), 0.86 (t, J = 6.8 Hz, 3 H, Ar(CH₂)₁₄Me); ¹³C NMR (75 MHz, CDCl₃): δ 171.6, 165.2, 160.3, 148.9, 110.8, 105.1, 101.4, 61.4, 37.0, 32.0, 31.9, 29.9, 29.7, 29.3, 22.7, 14.1; EIMS (m/z, %): 123 (13.3), 150 (20.1), 163 (28.6), 164 (14.0), 177 (16.1), 196 (100.0), 197 (11.5), 392 (13.1); Anal. Calcd for C₂₄H₄₀O₄: C, 73.47; H 10.20. Found: C, 73.18; H 10.29.

Compound 17: Rf 0.67 (petroleum ether: EtOAc = 7:1); ¹H NMR (300 MHz, CDCl₃): δ 11.86 (s, 1 H, OH), 6.32 (d, J = 2.7 Hz, 1 H, ArH), 6.27 (d, J = 2.7 Hz, 1 H, ArH), 4.38 (q, J = 7.2 Hz, 2 H, OCH₂), 3.79 (s, 3 H, OMe), 2.84 (t, J = 7.7 Hz, 2 H, ArCH₂), 1.56-1.54 (m, 2 H, ArCH₂CH₂), 1.41 (t, J = 7.1 Hz, 3 H, CO₂CH₂Me), 1.26 (m, 24 H, Ar(CH₂)₂(CH₂)₁₂), 0.86 (t, J = 6.8 Hz, 3 H, Ar(CH₂)₁₄Me); ¹³C NMR (75 MHz, CDCl₃): δ 171.6, 165.6, 163.8, 148.0, 110.6, 104.8, 98.8, 61.2, 55.2, 37.0, 32.0, 31.9, 29.9, 29.7, 29.3, 22.7, 14.1; EIMS (m/z, %): 137 (11.5), 138 (11.7), 164 (22.3), 177 (24.2), 210 (100.0), 211 (12.3), 406 (12.9); Anal. Calcd for C₂₅H₄₂O₄: C, 73.89; H, 10.34. Found: C, 73.71; H 10.53.

2,4-Bis(benzyloxy)-6-pentadecanylbenzoic acid (19)

![Structure](image)

To a solution of 16 (1.02 g, 2.60 mmol) in dry acetone (20 mL) was added K₂CO₃ (1.04 g, 3.0 eq) and BnBr (0.9 mL, 3.0 eq). The mixture was heated to reflux for 12 h. The solution was then diluted with EtOAc (50 mL), washed with water and brine, respectively. The organic phase was dried over Na₂SO₄ and concentrated to give the crude 18.

A solution of the crude 18 and KOH (420 mg) in DMSO (10 mL) and H₂O (1.0 mL) was heated at 90 °C for 24 h. Then the solution was acidified with 1 N HCl (20 mL), and extracted with CH₂Cl₂ (30 mL × 3). The organic phase was washed with brine (20 mL), and then was dried and concentrated. The residue was applied to chromatography over silica gel (petroleum ether : EtOAc = 8:1), affording acid 19 (1.40 g, 99%) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ 7.42-7.34 (m, 10 H, PhH), 6.51 (d, J = 2.4 Hz, 1 H, S11
Benzyl 4’-(2,4-dibenzyloxy-6-pentadecanylbenzoyloxy)-2’-hydroxy-6’-methylbenzoate (20)

To a solution of acid 19 (300 mg, 0.55 mmol) and phenol 11 (140 mg, 0.55 mmol) in dry toluene (5 mL) was slowly added (CF₃CO)₂O (0.7 mL). After stirring for 2 h at room temperature, the mixture was concentrated. The residue was applied to chromatography over a short column of silica gel (petroleum ether : EtOAc = 8:1) to give 20 (406 mg, 94%) as a yellow oil. Rₛ 0.59 (petroleum ether : EtOAc = 4:1); ¹H NMR (300 MHz, CDCl₃): δ 11.55 (s, 1 H, OH), 7.43-7.32 (m, 15 H, PhH), 6.63 (d, J = 2.1 Hz, 1 H, ArH), 6.52 (d, J = 2.1 Hz, 1 H, ArH), 6.49 (d, J = 2.1 Hz, 1 H, ArH), 6.39 (d, J = 2.4 Hz, 1 H, ArH), 5.41 (s, 2 H, OCH₂), 5.08 (s, 4 H, 2 PhCH₂), 2.69 (t, J = 7.8 Hz, 2 H, ArCH₂), 2.44 (s, 3 H, ArCH₃), 1.65 (t, J = 7.2 Hz, 2 H, ArCH₂H₂), 1.26 (m, 24 H, Ar(CH₂)₂(CH₂)₁₂), 0.89 (t, J = 6.8 Hz, 3 H, Ar(CH₂)₁₄Me); ¹³C NMR (75 MHz, CDCl₃): δ 171.1, 166.0, 164.5, 160.9, 157.6, 155.2, 143.9, 143.2, 136.4, 136.3, 135.1, 128.7, 128.6, 128.5, 128.2, 128.1, 127.5, 116.7, 115.6, 109.9, 108.8, 107.4, 98.2, 70.7, 70.2, 67.4, 33.9, 31.9, 31.8, 31.3, 29.7, 29.5, 29.3, 24.4, 22.7, 14.1; ESIMS (m/z) for C₅₁H₆₉O₇ [M + Na⁺]: 807.5; Anal. Calcd for C₅₁H₆₉O₇: C, 78.06; H, 7.65. Found: C, 77.89; H, 7.75.
Compound 20 (400 mg, 0.51 mmol) was treated with 10% Pd/C (50 mg) in EtOAc (10 mL) under 1 atm H₂ atmosphere for 4 days. The mixture was then filtered and concentrated. The residue was purified by chromatography over a short column of silica gel (CH₂Cl₂ : MeOH = 15: 1) to give 21 (262 mg, 100%) as a white solid. Rₓ 0.33 (CH₂Cl₂ : MeOH = 15:1). ¹H NMR (CD₃COCD₃): δ 11.07 (s, 1 H, OH), 6.76 (s, 1 H, ArH), 6.74 (s, 1 H, ArH), 6.39 (d, J = 2.1 Hz, 1 H, ArH), 6.29 (d, J = 1.8 Hz, 1 H, ArH), 2.92 (t, J = 7.1 Hz, 2 H, ArCH₂), 2.63 (s, 3 H, ArCH₃), 1.65 (t, J = 7.7 Hz, 2 H, ArCH₂CH₂), 1.24-1.20 (m, 24 H, Ar(CH₂)₂(CH₂)₁₂), 0.84 (t, J = 6.6 Hz, 3 H, Ar(CH₂)₁₄Me); ESIMS (m/z) for C₃₀H₄₂O₇ [M + Na⁺]: 537.3; HR-ESIMS (m/z) Calcd for C₃₀H₄₂O₇ [M + Na⁺]: 537.2833; Found: 537.2823.

Benzyl 4’-(2,4-dihydroxy-6-pentadecanylbenzoyloxy)-2’-hydroxy-6’-methylbenzoate (22)

To a solution of 21 (245 mg, 0.48 mmol) in dry DMF (10 mL) was added KHCO₃ (57 mg, 1.2 eq) and BnBr (0.074 mL, 1.3 eq). After stirring at room temperature for 40 h, the mixture was diluted with EtOAc (50 mL). The organic phase was washed with water and brine, respectively, and was then dried over Na₂SO₄ and concentrated. The residue was subjected to chromatography over silica gel (petroleum ether : EtOAc = 6:1) to give 22 (256 mg, 89%) as a yellow oil. Rₓ 0.50 (petroleum ether : EtOAc = 4:1); ¹H NMR (300 MHz, CDCl₃): δ 11.66 (s, 1 H, OH), 11.35 (s, 1 H, OH), 7.46-7.37 (m, 5 H, PhH), 6.70 (d, J = 2.4 Hz, 1 H, ArH), 6.56 (d, J = 2.1 Hz, 1 H, ArH), 6.31 (s, 1 H, ArH), 6.30 (s, 1 H, ArH), 6.25 (br s, 1 H, OH), 5.43 (s, 2 H, OCH₂), 2.92 (t, J = 7.7 Hz, 2 H, ArCH₂), 2.56 (s, 3 H, ArCH₃), 1.62 (t, J = 7.2 Hz, 2 H, ArCH₂CH₂), 1.28-1.25 (m, 24 H, ArCH₂CH₂),
Ar(CH$_2$)$_2$(CH$_2$)$_{12}$), 0.88 (t, $J$ = 6.8 Hz, 3 H, Ar(CH$_2$)$_{12}$Me); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 171.1, 169.5, 166.0, 164.4, 161.5, 153.9, 149.4, 143.6, 134.9, 128.7, 128.6, 128.5, 116.6, 111.6, 110.4, 108.7, 103.8, 101.6, 67.6, 37.1, 32.1, 31.9, 29.8, 29.6, 29.3, 24.4, 22.6, 14.1; ESIMS ($m/z$) for C$_{37}$H$_{48}$O$_7$ [M + Na$^+$]: 627.4; Anal. Calcd for C$_{37}$H$_{48}$O$_7$: C, 73.51; H, 7.95. Found: C, 73.17; H, 7.96.

**Benzyl 4’-(4-O-(2’’,3’’-di-O-acetyl-4’’,6’’-O-benzylidene-β-D-glucopyranosyl)-2-hydroxy-6-pentadecanylbenzoyloxy)-2’-hydroxy-6’-methylbenzoate (23)**

A mixture of phenol 22 (229 mg, 0.46 mmol), glycosyl imidate 8 (232 mg, 0.384 mmol), and 4Å MS (150 mg) in anhydrous CH$_2$Cl$_2$ (5.0 mL) was stirred at ambient temperature for 30 min before cooling to 0 °C. And then BF$_3$·OEt$_2$ (0.49 mL, 0.158 M in CH$_2$Cl$_2$, 0.2 eq) was added slowly. After stirring for another 20 min at 0 °C, the mixture was warmed to ambient temperature and stirred overnight. The reaction mixture was quenched by addition of saturated aqueous NaHCO$_3$ and diluted with CH$_2$Cl$_2$ and additional saturated aqueous NaHCO$_3$. The organic phase was separated, washed with water, and then dried over Na$_2$SO$_4$ and concentrated. The residue was purified by silica gel column chromatography (petroleum ether : EtOAc = 6:1) to afford 23 (196 mg, 55%) as a white foam. $R_f$ 0.44 (petroleum ether : EtOAc = 4:1); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 11.63 (s, 1 H, OH), 11.28 (s, 1 H, OH), 7.47-7.37 (m, 5 H, PhH), 6.70 (d, 1 H, $J$ = 1.8 Hz, ArH), 6.56 (d, 1 H, $J$ = 2.4, ArH), 6.49 (d, 1 H, $J$ = 2.7 Hz, ArH), 6.43 (d, 1 H, $J$ = 2.4 Hz, ArH), 5.55 (s, 1 H), 5.43 (s, 2 H), 5.30 (m, 2 H), 4.43 (m, 1 H), 3.88-3.75 (m, 3 H), 2.95 (m, 2 H), 2.08 (s, 6 H), 1.64 (m, 2 H, ArCH$_2$CH$_2$), 1.28-1.24 (m, 24 H, Ar(CH$_2$)$_{12}$Me), 0.89 (t, $J$ = 6.8 Hz, 3 H, Ar (CH$_2$)$_{12}$Me); ESIMS ($m/z$): 961.5 (M + Na$^+$); HR-ESIMS ($m/z$) Calcd for C$_{54}$H$_{66}$O$_{14}$Na$: 961.4345; Found: 961.4344.
Benzyl 4’-(4-O-(2’’,3’’-di-O-acetyl-β-D-glucopyranosyl)-6-pentadecanoylbenzoyloxy)-2’-benzyloxy-6’-methylbenzoate (24)

To a solution of 23 (180 mg, 0.192 mmol) in dry acetone (10 mL) was added K₂CO₃ (106 mg, 4.0 eq) and BnBr (0.1 mL). The mixture was heated to reflux for 12 h and then was diluted with EtOAc (50 mL). The organic phase was washed with water and brine, dried over Na₂SO₄, and concentrated. The residue was subjected to column chromatography over silica gel (petroleum ether : EtOAc = 4:1) to provide 24 (171 mg, 80%) as a white foam. Rf 0.46 (petroleum ether : EtOAc = 4:1); ¹H NMR (300 MHz, CDCl₃): δ 7.37-7.22 (m, 20 H), 6.62 (d, 1 H, J = 2.4 Hz, ArH), 6.40 (d, 1 H, J = 2.1 Hz, ArH), 6.36 (d, 1 H, J = 2.4 Hz, ArH), 6.31 (d, 1 H, J = 1.5 Hz, ArH), 5.50 (s, 1 H), 5.40-5.32 (m, 3 H), 5.25 (d, 1 H, J = 7.5 Hz), 5.20 (s, 2 H), 5.10 (d, 1 H, J = 7.8 Hz), 4.92 (s, 2 H), 4.30 (q, 1 H, J = 4.8 Hz), 3.81-3.73 (m, 2 H), 3.63 (m, 1 H), 2.58 (t, 1 H, J = 8.1 Hz), 2.21 (s, 3 H), 2.06 (s, 3 H), 2.22 (s, 3 H), 1.60-1.50 (m, 2 H), 1.26 (m, 24 H, Ar(CH₂)₁₂), 0.88 (t, J = 6.8 Hz, 3 H, Ar(CH₂)₁₂Me); ¹³C NMR (75 MHz, CDCl₃): δ 170.0, 169.4, 167.6, 166.6, 158.5, 157.9, 157.0, 154.4, 144.3, 138.4, 136.5, 136.2, 135.6, 135.2, 129.1, 128.47, 128.41, 128.37, 128.35, 128.2, 128.1, 127.8, 127.2, 126.9, 121.5, 119.2, 113.2, 111.7, 106.0, 101.5, 101.0, 98.9, 77.8, 71.9, 71.5, 70.3, 68.2, 67.2, 66.9, 66.4, 33.6, 31.8, 31.1, 29.6, 29.5, 29.43, 29.36, 29.28, 22.6, 20.7, 20.5, 19.5, 14.1; ESIMS (m/z): 1141.7 (M + Na⁺), 1158.0 (M + K⁺); HR-ESIMS (m/z) Calcd for C₆₈H₇₆O₁₄Na⁺: 1141.5290; Found: 1141.5284.

Benzyl 4’-(4-O-(2’’,3’’-di-O-acetyl-β-D-glucopyranosyl)-2-benzyloxy-6-pentadecanoylbenzoyloxy)-2’-benzyloxy-6’-methylbenzoate (25)
A solution of 24 (211 mg, 0.189 mmol) in 90% HOAc (5 mL) in the presence of p-TsOH (4 mg, 0.1 eq) was stirred at 40 °C for 6 h. The solution was diluted with EtOAc (50 mL). The organic phase was washed with water and brine, dried over Na₂SO₄, and concentrated. The residue was subjected to silica gel column chromatography (petroleum ether : EtOAc = 2:1) to provide 25 (100 mg, 51%) as a white foam. Rf 0.51 (petroleum ether : EtOAc = 1:1); ¹H NMR (300 MHz, CDCl₃): δ 7.37-7.25 (m, 15 H), 6.58 (d, 1 H, J = 1.8, ArH), 6.45 (d, 1 H, J = 1.5 Hz, ArH), 6.37 (s, 1 H), 6.26 (d, 1 H, J = 1.8 Hz, ArH), 5.34 (s, 2 H), 5.22 (s, 2 H), 5.11 (m, 2 H), 4.94 (m, 3 H), 3.82-3.65 (m, 3 H), 3.37 (m, 1 H), 3.35-3.30 (m, 1 H), 2.58 (t, 1 H, J = 8.1 Hz), 2.50-2.42 (br, 1 H), 2.21 (s, 3 H), 2.09 (d, 3 H, J = 2.1 Hz), 2.02 (s, 6 H), 1.60-1.50 (m, 2 H), 1.26 (m, 24 H, Ar (CH₂)₂ (CH₃)₁₂), 0.89 (t, J = 6.8 Hz, 3 H, Ar(CH₂)₁₂Me); ¹³C NMR (75 MHz, CDCl₃): δ 171.3, 169.5, 168.1, 166.8, 158.2, 158.0, 157.0, 155.1, 144.3, 138.4, 136.1, 135.3, 135.0, 128.5, 128.4, 128.3, 128.2, 128.0, 127.3, 120.5, 119.6, 112.8, 112.7, 104.4, 101.8, 98.2, 75.5, 75.2, 70.8, 70.4, 69.7, 67.2, 62.2, 33.7, 31.9, 29.67, 29.56, 29.51, 29.4, 29.3, 22.7, 20.8, 20.6, 19.5, 14.1; ESIMS (m/z): 1053.8 (M + Na⁺), 1069.8 (M + K⁺); HR-ESIMS (m/z) Calcd for C₆₁H₇₄O₁₄Na⁺: 1053.4977; Found: 1053.4971.

2,4-Dihydroxy-6-pentadecanylbenzoic acid (26)

Compound 19 (794 mg, 1.46 mmol) was treated with 10%Pd/C (100 mg) in EtOAc (20 mL) under 1 atm H₂ atmosphere for 5 h. The mixture was then filtered and concentrated. The residue was subjected to chromatography over a short column of silica gel (petroleum ether : EtOAc = 4:1 to 1:2) to provide 26 (526 mg, 99%) as a white foam. ¹H NMR (300 MHz, CD₃COCD₃): δ 6.30 (s, 1 H, ArH), 6.23 (s, 1 H, ArH), 2.93 (t, 1 H, J =
7.8 Hz), 1.62-1.58 (m, 2 H), 1.35-1.26 (m, 24 H, Ar(CH2)2(CH2)12), 0.89 (t, J = 6.8 Hz, 3 H, Ar(CH2)12Me).

**Benzyl 2,4-dihydroxy-6-pentadecanylbenzoate (27)**

![Chemical Structure](image)

To a solution of 26 (524 mg, 1.44 mmol) in dry DMF (5 mL) was added KHCO3 (173 mg, 1.2 eq) and BnBr (0.2 mL, 1.15 eq). The mixture was heated to reflux for 40 h. The solution was diluted with EtOAc (50 mL). The organic phase was washed with water and brine, respectively, and was then dried over Na2SO4 and concentrated. The residue was purified by silica gel column chromatography (petroleum ether : EtOAc = 6:1) to provide 27 (575 mg, 88%) as a white solid. Rf 0.33 (petroleum ether : EtOAc = 4: 1); 1H NMR (300 MHz, CDCl3): δ 11.74 (s, 1 H, OH), 7.42-7.37 (m, 5 H, ArH), 6.26 (d, 1 H, J = 2.4 Hz, ArH), 6.19 (d, 1 H, J = 2.7 Hz, ArH), 5.34 (s, 2H), 2.75 (t, 1 H, J = 8.1 Hz), 1.40-1.05 (m, 26 H, Ar(CH2)2(CH2)12), 0.88 (t, J = 6.8 Hz, 3 H, Ar(CH2)12Me); 13C NMR (75 MHz, CDCl3): δ 171.3, 165.4, 160.3, 149.2, 134.9, 129.0, 128.7, 110.8, 104.9, 101.3, 67.4, 37.0, 32.1, 31.9, 29.7, 29.61, 29.58, 29.4, 22.7, 14.1; IR (KBr): 3375, 2918, 1647, 1466, 1265, 1162, 1104, 696 cm⁻¹; ESIMS (m/z): 453.3 (M - H⁻); HR-ESIMS (m/z) Calcd for C29H41O4⁻: 453.3003; Found: 453.3010; Anal. Calcd for C29H42O4: C, 76.61; H, 9.31. Found: C, 76.43; H, 9.32.

**Benzyl 2-hydroxy-4-(methoxymethoxy)-6-methylbenzoate (28)**

![Chemical Structure](image)

To a solution of 11 (459 mg, 1.78 mmol) in CH2Cl2 (5.0 mL) was added i-Pr2NEt (0.62 mL, 2.0 eq) and MOMCl (0.14 mL, 1.1 eq) at room temperature. After stirring overnight, the solution was diluted with CH2Cl2 (50 mL), and was then washed with water and brine, respectively. The organic phase was dried over Na2SO4 and concentrated. The residue
was subjected to silica gel column chromatography (petroleum ether : EtOAc = 8:1) to provide 28 (494 mg, 92%) as a white solid. Rf 0.58 (petroleum ether : EtOAc = 4: 1); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 11.68 (s, 1 H, OH), 7.42-7.36 (m, 5 H, ArH), 6.49 (d, 1 H, \(J = 2.4\) Hz, ArH), 6.37 (d, 1 H, \(J = 2.4\) Hz, ArH), 5.38 (s, 2 H), 5.17 (s, 2 H), 3.45 (s, 3 H), 2.49 (s, 3 H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 171.4, 165.3, 161.4, 143.4, 135.3, 128.6, 128.41, 128.38, 111.8, 106.1, 101.5, 93.8, 67.0, 56.2, 24.6; IR (KBr): 2979, 1645, 1324, 1263, 1161, 1022, 936 cm\(^{-1}\); EIMS (\(m/z\)): 302 (M\(^+\)); Anal. Calcd for C\(_{17}\)H\(_{18}\)O\(_5\): C, 67.54; H, 6.00. Found: C, 67.50; H, 6.01.

**Benzyl 2-benzyloxy-4-methoxymethoxy-6-methylbenzoate (29)**

![](image)

To a solution of 28 (490 mg, 1.62 mmol) in dry acetone (5 mL) was added K\(_2\)CO\(_3\) (614 mg, 2.5 eq) and BnBr (0.4 mL, 1.8 eq). The mixture was heated to reflux for 12 h, and was then diluted with EtOAc (50 mL). The organic phase was washed with water and brine, respectively, and was then dried over Na\(_2\)SO\(_4\) and concentrated. The residue was subjected to silica gel column chromatography (petroleum ether : EtOAc = 10:1) to provide 29 (566 mg, 89%) as a colorless oil. Rf 0.42 (petroleum ether : EtOAc = 4: 1); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.34-7.26 (m, 10 H, ArH), 6.49 (s, 1 H, ArH), 6.48 (s, 1 H, ArH), 5.31 (s, 2 H), 5.13 (s, 2 H), 5.05 (s, 2 H), 3.43 (s, 3 H), 2.27 (s, 3 H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 168.0, 158.8, 157.1, 138.3, 136.5, 135.8, 128.42, 128.40, 128.35, 128.1, 127.8, 127.2, 117.7, 109.6, 99.1, 94.2, 70.3, 66.0, 56.0, 19.8; IR (KBr): 2955, 1726, 1605, 1588, 1455, 1264, 1149, 1096, 1031, 736 cm\(^{-1}\); EIMS (\(m/z\)): 302 (M\(^+\)); Anal. Calcd for C\(_{24}\)H\(_{24}\)O\(_5\): C, 73.45; H, 6.16. Found: C, 73.57; H, 6.25.

**Benzyl 2-benzyloxy-4-hydroxy-6-methylbenzoate (30)**

![](image)
To a solution of 29 (550 mg, 1.40 mmol) in THF (5 mL) was added 6 N HCl (2.5 mL). After stirring at room temperature for 3 h, the solution was diluted with saturated aqueous NaHCO₃ and extracted twice with EtOAc (50 mL). The organic phase was washed with water and brine, respectively, and was then dried over Na₂SO₄ and concentrated. The residue was subjected to silica gel column chromatography (petroleum ether : EtOAc = 6:1) to give 30 (415 mg, 85%) as a colorless oil. Rᵣ 0.25 (petroleum ether : EtOAc = 4: 1); ¹H NMR (300 MHz, CDCl₃): δ 7.52 (br s, 1 H), 7.32-7.22 (m, 10 H, ArH), 6.24 (d, 1 H, J = 1.8 Hz, ArH), 6.15 (d, 1 H, J = 1.5 Hz, ArH), 5.28 (s, 2 H), 4.80 (s, 2 H), 2.13 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 169.6, 158.4, 157.6, 138.7, 136.4, 135.5, 128.6, 128.49, 128.47, 128.3, 127.9, 127.3, 115.0, 109.7, 98.3, 70.2, 67.4, 19.8; IR (KBr): 3370, 1696, 1606, 1455, 1270, 1166, 1090, 838, 736 cm⁻¹; EIMS (m/z): 348 (M⁺); HR-FTMS (m/z) Calcd for C₂₂H₂₁O₄: 349.1442; Found: 349.1434.
c13
yubj4087 in cdcl3
Pulse Sequence: 62pm1
Yubj5004
in CDCl3
Nov. 25, 2003

5
Cl3

Pulse Sequence: s2pu1

[Chemical structure image]

200 180 160 140 120 100 80 60 40 20 ppm
c13
yubj4125 in cdcl3
Pulse Sequence: s2pul

[Chemical Structure Image]
C13

yubj4129 in cdcl3

Pulse Sequence: s2pul
c13
yubj4135 in cdcl3
Pulse Sequence: s2pul
w1337

\[
\begin{align*}
\text{Structure:} & \\
\text{Chemical Shift:} & \\
\text{S33}
\end{align*}
\]
w1344

24

S39
Pulse Sequence: s2pul
c13
W101 in cdcl3
Pulse Sequence: 52pyt

33

S54
w1481
CD3COCD3-MeOD

35
C13

W1427 in acetone

Pulse Sequence: t2pul